THE ANALYST.

MAY, 1901.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The monthly meeting of the Society was held on Wednesday evening, April 3, in the Chemical Society's Rooms, Burlington House.

In the absence of the President through indisposition, Mr. Otto Hehner occupied the chair.

The minutes of the previous meeting were read and confirmed.

Professor T. E. Thorpe, C.B., D.Sc., F.R.S., was elected an honorary member of the Society; and Messrs. H. Wippell Gadd and Albert H. Mitchell, B.Sc., were elected members.

A certificate of proposal for election to membership in favour of Mr. John Webster was read for the second time.

The following papers were read: "On the Maumené Test for Oils," by C. A. Mitchell, B.A.; "Some Arsenic Estimations relating to Malt Kilns," by Thomas Fairley; "On Gutzeit's Test for Arsenic," by F. C. J. Bird; and "The Aeration Test for Effluents," by S. Rideal, D.Sc.

COMPOSITION OF DUTCH BUTTER.

By John Clark, Ph.D.

(*Read at the Meeting, February* 5, 1901.)

During the last five years I have had occasion to analyse a large number of butters, all of which are certified by the importers as being derived from factories in Friesland, a province in the north of the Netherlands, in which, I understand, no margarine is manufactured. As each sample represents a shipment, I have thought it would be of some interest to publish the results which I have obtained, to show the extent to which the volatile acids in the fat may fall in butters the genuineness of which seems to be beyond question. All the results were obtained by Leffmann and Beam's alkali-glycerin process, which, in my opinion, is quite as accurate as the Reichert-Wollny method and more expeditious. A blank was made with the alkali-glycerin, and the distillation was carried to about one-fourth of the original volume. In most cases I employed a slight excess of sulphuric acid to decompose the soap, but I have found by numerous experiments that the same results are obtained when a considerable excess of phosphoric acid is used for this purpose. The volatile acids, after deducting the blank, are given in their equivalent of butyric acid:

Year.	Month.	Number of Samples.	Volatile Acids Per Cent. Average.	Maximum.	Minimum.
1896	January ...	3	4·90	5·06	4·80
	February ...	5	5·17	5·52	4·80
	March ...	4	5·50	5·57	5·44
	April	1	5·54		
	May	2	5·27	5·36	5·18
	June	None			
	July	3	5·26	5·29	5·13
	August ...	4	5·37	5·50	5·24
	September ...	None			
	October ...	1	4·75		
	November ...	1	4·70		
	December ...	1	5·34		
1897	January ...	1	4·90		
	February ...	3	5·37	5·72	4·99
	March ...	1	4·96		
	April	None			
	May	2	5·50	5·72	5·28
	June	2	5·45	5·54	5·36
	July	None			
	August ...	1	5·44		
	September ...	None			
	October ...	1	5·00		
	November ...	2	4·73	4·90	4·57
	December ...	1	5·50		
1898	January ...	None			
	February ...	2	5·14	5·18	5·10
	March ...	None			
	April	None			
	May	None			
	June	5	5·55	5·90	5·01
	July	1	4·84		
	August ...	2	5·16	5·48	4·85
	September ...	3	4·96	5·08	4·81
	October ...	4	4·79	5·01	4·45
	November ...	9	4·88	5·14	4·62
	December ...	2	4·97	5·15	4·80
1899	January ...	2	5·15	5·20	5·10
	February ...	1	5·15		
	March ...	2	5·74	5·86	5·63
	April	3	5·88	6·06	5·80
	May	1	5·90		
	June	None			
	July	1	5·50		
	August ...	8	5·16	5·83	4·84
	September ...	3	5·15	5·20	5·05
	October ...	4	4·92	5·12	4·71
	November ...	6	4·77	5·04	4·43
	December ...	None			

Year.	Month.	Number of Samples.	Volatile Acids Per Cent. Average.	Maximum.	Minimum.
1900	January ...	1	5·20		
	February ...	2	5·15	5·20	5·10
	March ...	3	5·65	5·96	5·40
	April	5	5·56	5·80	5·30
	May	None			
	June	3	5·45	5·74	5·30
	July	1	5·12		
	August ...	4	5·12	5·35	4·77
	September ...	16	4·80	5·17	4·45
	October ...	29	4·76	5·25	4·35
	November ...	34	4·67	5·18	4·20
	December ...	3	4·76	4·86	4·64

The above analyses indicate that the volatile acids in Friesland butter by this method are, on an average, 5·17 per cent. On seven occasions they fell below 4·5 per cent., but in several of these cases I have been able to prove the genuineness of the butter. In 1898 the sample giving 4·45 per cent. of volatile acids was reported as of doubtful purity, and for the satisfaction of the importers I was requested to send someone to visit the factory in which the butter was made. For this purpose I nominated Mr. B. A. van Ketel, analyst in Amsterdam, who forwarded to me a sample of butter, which he certified was churned in his presence, and a portion of the cream from which it was made. The analyses of the fat of each of these gave the following results :

	Butter Fat.	Cream Fat.
Volatile acids per cent.	4·42	4·45

In October of last year two samples of butter from different factories showing 4·35 per cent. of volatile acids were also reported as of doubtful purity, and to satisfy the importers I again asked Mr. van Ketel to visit these factories, and send me samples of the butter and of the cream. On analysis the fats of these gave the following results :

	No. 1. Butter.	No. 1. Cream.	No. 2. Butter.	No. 2. Cream.
Volatile acids per cent.	4·30	4·35	4·33	4·33

In November two of the butters gave only 4·2 and 4·22 per cent. of volatile acids, and although I had no opportunity in these cases of examining certified samples from the churn, I received a letter from Dr. K. H. M. v. d. Lande, Director of the Government Agricultural Station at Hoorn, stating that on November 10 he had analysed a sample of butter from the same factory, taken from the churn in presence of witnesses, and that he found it to contain 4·19 per cent. of volatile acid, calculated as butyric acid.

The above results indicate that the poverty in volatile acid in these cases is not due to adulteration, but to natural causes, and this seems to take place mainly from about the middle of September till the middle of November, and is said to be due to the exposure of the cattle to the cold, combined with indifferent feeding, as the proportion of volatile acid gradually increases after the cattle are housed.

Discussion.

Mr. Hehner said that it was very difficult to discuss such a paper as this in the absence of the author. He would have liked to ask what the author meant when he spoke of volatile acids. He gathered that the process used was practically the Wollny process, excepting that the saponification was carried out according to Leffmann's method, with sodium hydroxide and glycerin. It was, however, practically impossible to distil off completely the volatile fatty acids, and as no correction appeared to have been made for that portion of the acids which did not distil over, the figures would be simply the Wollny figures, multiplied by a factor for conversion into percentages of volatile fatty acids. Unfortunately, the results of such processes were ordinarily recorded, not in percentages of volatile fatty acids, but in c.c. of decinormal alkali neutralized by a given quantity of butter. It would have been much more satisfactory if a system of the kind followed in this paper had been adopted from the first : as it was, it was almost impossible to form any opinion on the figures as they stood. For many years past the Dutch butter importers had been up in arms every November against analysts in England who condemned samples representing consignments of Dutch butter, which were said to be perfectly genuine. There was no doubt that this state of things was in a great measure due to the fact that in Holland the calving of the cows was managed in a preposterously bad manner. The cows somehow or other were allowed to get dry all at the same time, and consequently all at the same time to reach a condition in which the fat of their milk was quite abnormal in composition. This occurred at about the end of October or the beginning of November, just at the same time at which the change took place from the open air to stall feeding, a change which deeply affected the composition of the butter-fat. Taking these two circumstances together, it might very well happen, apart from any question of fraud, that the butter might analyse abnormally ; but no such fluctuations would occur if the Dutch farmers chose to arrange that the calving of their cows was fairly divided over the year, as was the case in any country where farming was reasonably conducted, and if they stabled their cows rather earlier than hitherto. He understood that this matter was now being discussed by the more intelligent of the Dutch farmers themselves. As a result of this unfortunate management, and the difficulties which arose in consequence, Dutch butter had become discredited to such an extent that the Belgian Government now enacted that no butter should be exported from Belgium which gave a Reichert-Wollny figure lower than 25.

Mr. Bevan said it seemed quite clear that the process which Dr. Clark had used was analogous to the Reichert-Wollny process, and he thought it quite right to assume, therefore, that the figures were comparable with the Reichert-Wollny figures expressed in terms of c.c. of decinormal alkali.

Dr. Dyer said that he would have liked to ask Dr. Clark to restate these figures in what were now the usual terms. He thought that Mr. Hehner's view was probably correct as to the curious arbitrary method of statement which was used in the Reichert process ; but that method of statement was now so universally adopted that it did not seem desirable to change it. He did not agree that it would be better to state the results in terms of the volatile acids, for, in speaking of percentages of

volatile acids, the calculation was made on the assumption (which of course was also arbitrary) that the volatile fatty acids all consisted of butyric acid, which was not the case; whereas the Reichert figure was at least a statement of fact, viz., that a certain quantity of butter yielded under certain circumstances a quantity of volatile fatty acids represented by a certain quantity of standard alkali.

(The following reply to some of the points in the discussion has been received from Dr. Clark.—Ed.)

The "volatile acids" are stated in terms of butyric acid, and are calculated from the Reichert-Wollny figures. They represent the volatile acids distilled over, *not* the total volatile or butyric acid. This is the manner in which I always report my butter analyses, and is one more easily understood by a court. The process employed is analogous to the Reichert-Wollny process, and the results given can be converted into the Reichert-Wollny figures, expressed in terms of c.c. of decinormal alkali, by multiplying the volatile acids by 5·682. In this way it will be found that 4·4 per cent. of butyric or volatile acid corresponds to the Reichert-Wollny figure 25.

THE PHYSICAL STATE IN WHICH FAT EXISTS IN CREAM.

By H. Droop Richmond, F.I.C., and Sylvester Oliffe Richmond.

(*Read at the Meeting, February* 5, 1901.)

One of us has already shown that there is a distinct change of density of cream at about the melting-point of the fat ("Dairy Chemistry," Appendix A., pp. 338-341); it was further shown that separated milk exhibits no such change, and that the expansion of the fat in cream agrees with the expansion of butter-fat, assuming that it is liquid above its melting-point and solid below that. This is true of cream that has been kept for some hours at a low temperature, and does not hold with cream that has been heated and rapidly cooled; the density results point to the assumption that the solidification of the fat is a process which goes on only slowly.

As the density gives only indirect evidence, and as it has been concluded by several authorities that the fat in milk is always liquid, we have thought it desirable to study the question in another way.

If a body is receiving heat from any source, the rate of rise of temperature will depend (*a*) on the difference of temperature, and (*b*) on the specific heat-capacity; if at any point a change involving absorption or evolution of heat takes place, the curve of temperature will show discontinuity at that point, and if, in addition, the change causes an alteration of specific heat-capacity, there will not only be discontinuity, but also a change of curvature at that point.

As it is extremely unlikely that the specific heat capacities of solid and liquid fat are the same, we should expect to find a change of the rate of heating at the melting-point of fat.

The method adopted was to place about 20 c.c. of cream in a tube in which were a thermometer reading directly to $\frac{1}{10}^{\circ}$ C., and by estimation to $\frac{1}{100}^{\circ}$ C., and a stirrer;

TABLE I.

Series I.—Well-cooled Cream.

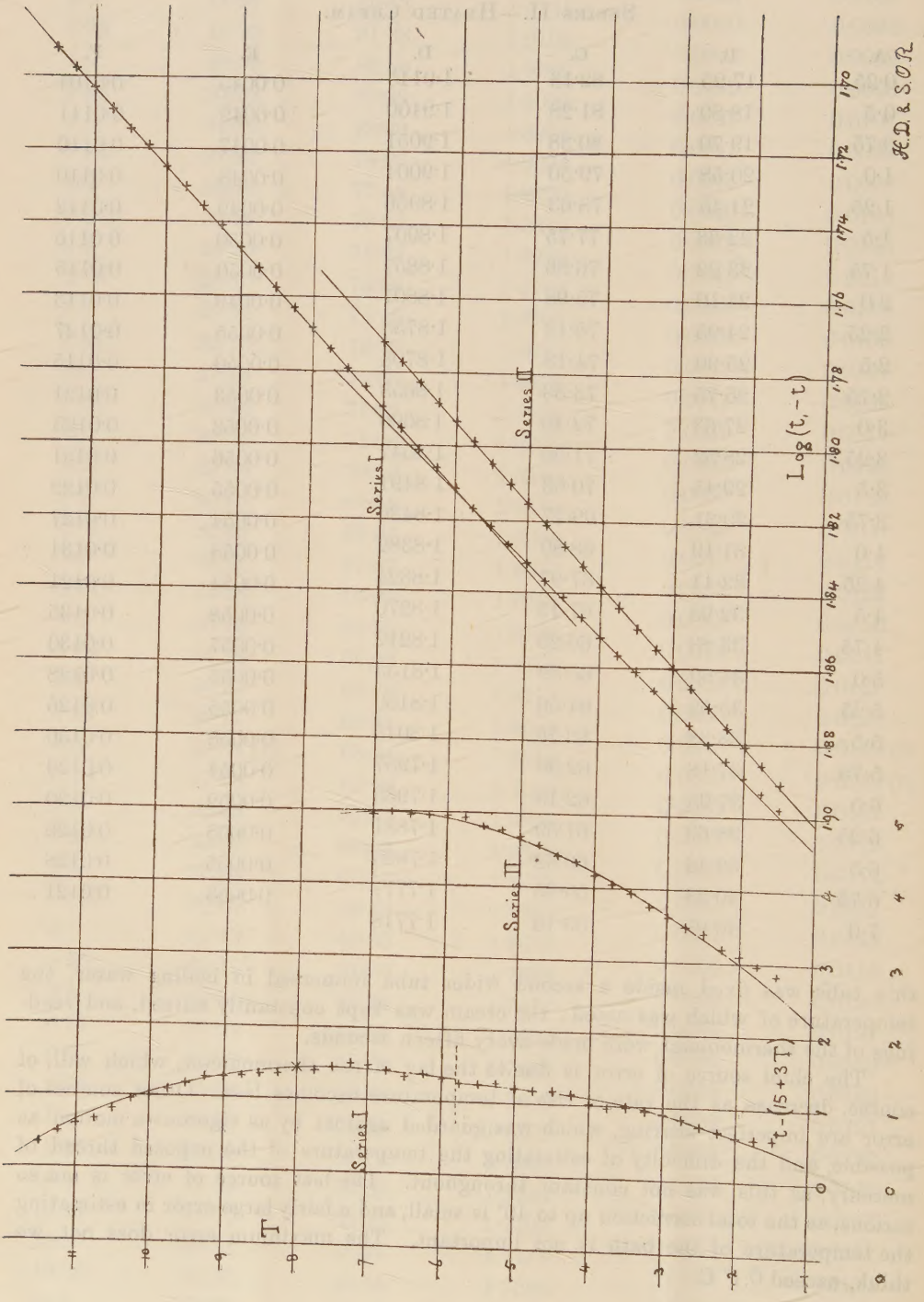
A.	B.	C.	D.	E.	F.
0·25	17·28	82·80	1·9180	0·0035	0·0081
0·5	17·95	82·13	1·9145	0·0040	0·0092
0·75	18·70	81·38	1·9105	0·0043	0·0099
1·0	19·50	80·58	1·9062	0·0040	0·0093
1·25	20·25	79·83	1·9022	0·0047	0·0107
1·5	21·10	78·98	1·8975	0·0041	0·0095
1·75	21·85	78·23	1·8934	0·0044	0·0099
2·0	22·62	77·46	1·8890	0·0046	0·0108
2·25	23·45	76·63	1·8844	0·0045	0·0106
2·5	24·25	75·83	1·8799	0·0049	0·0112
2·75	25·10	74·98	1·8750	0·0048	0·0110
3·0	25·92	74·16	1·8702	0·0046	0·0106
3·25	26·70	73·38	1·8656	0·0047	0·0107
3·5	27·48	72·60	1·8609	0·0044	0·0102
3·75	28·22	71·86	1·8565	0·0048	0·0114
4·0	29·02	71·06	1·8517	0·0053	0·0124
4·25	29·90	70·18	1·8482	0·0050	0·0115
4·5	30·70	69·38	1·8412	0·0046	0·0106
4·75	31·43	68·65	1·8366	0·0049	0·0114
5·0	32·21	67·87	1·8317	0·0053	0·0122
5·25	33·03	67·05	1·8264	0·0048	0·0110
5·5	33·76	66·32	1·8216	0·0048	0·0111
5·75	34·49	65·59	1·8168	0·0055	0·0127
6·0	35·32	64·76	1·8113	0·0055	0·0127
6·25	36·14	63·94	1·8058	0·0048	0·0110 (?)
6·5	36·84 (?)	63·24	1·8010	0·0058	0·0140 (?)
6·75	37·68	62·40	1·7952	0·0057	0·0131
7·0	38·49	61·59	1·7895	0·0055	0·0126
7·25	39·26	60·82	1·7840	0·0049	0·0114
7·5	39·95	60·13	1·7791	0·0051	0·0117
7·75	40·65	59·43	1·7740	0·0057	0·0132
8·0	41·43	58·65	1·7683	0·0050	0·0115
8·25	42·10	57·98	1·7633	0·0056	0·0128
8·5	42·84	57·24	1·7577	0·0055	0·0127
8·75	43·56	56·52	1·7522	0·0056	0·0132
9·0	44·29	55·79	1·7466	0·0058	0·0133
9·25	45·03	55·05	1·7408	0·0053	0·0121
9·5	45·69	54·39	1·7355	0·0053	0·0122
9·75	46·35	53·73	1·7302	0·0053	0·0121
10·0	47·00	53·08	1·7249	0·0057	0·0133
10·25	47·70	52·38	1·7192	0·0051	0·0117
10·5	48·31	51·77	1·7141	0·0053	0·0120
10·75	48·93	51·15	1·7088	0·0059	0·0136
11·0	49·62	50·46	1·7029	0·0057	0·0126
11·25	50·25	49·83	1·6975	0·0052	0·0121
11·5	50·85	49·23	1·6923		

SERIES II.—HEATED CREAM.

A.	B.	C.	D.	E.	F.
0·25	17·95	82·13	1·9145	0·0045	0·0104
0·5	18·80	81·28	1·9100	0·0049	0·0111
0·75	19·70	80·38	1·9051	0·0047	0·0110
1·0	20·58	79·50	1·9004	0·0048	0·0110
1·25	21·45	78·63	1·8956	0·0049	0·0112
1·5	22·33	77·75	1·8907	0·0050	0·0115
1·75	23·22	76·86	1·8857	0·0050	0·0115
2·0	24·10	75·98	1·8807	0·0049	0·0113
2·25	24·95	75·13	1·8758	0·0055	0·0127
2·5	25·90	74·18	1·8703	0·0050	0·0115
2·75	26·75	73·33	1·8653	0·0053	0·0121
3·0	27·63	72·45	1·8600	0·0053	0·0125
3·25	28·52	71·56	1·8547	0·0056	0·0131
3·5	29·45	70·63	1·8491	0·0055	0·0122
3·75	30·31	69·77	1·8436	0·0054	0·0127
4·0	31·19	68·89	1·8382	0·0058	0·0134
4·25	32·11	67·97	1·8324	0·0054	0·0121
4·5	32·93	67·15	1·8270	0·0058	0·0135
4·75	33·83	66·25	1·8212	0·0057	0·0130
5·0	34·69	65·39	1·8155	0·0055	0·0128
5·25	35·52	64·56	1·8100	0·0055	0·0125
5·5	36·32	63·76	1·8045	0·0058	0·0136
5·75	37·18	62·90	1·7987	0·0054	0·0123
6·0	37·95	62·13	1·7933	0·0052	0·0120
6·25	38·69	61·39	1·7881	0·0055	0·0128
6·5	39·46	60·62	1·7826	0·0055	0·0128
6·75	40·23	59·85	1·7771	0·0053	0·0121
7·0	40·95	59·13	1·7718		

this tube was fixed inside a second wider tube immersed in boiling water, the temperature of which was noted; the cream was kept constantly stirred, and readings of the thermometer were made every fifteen seconds.

The chief source of error is due to the lag of the thermometer, which will, of course, decrease as the rate of rise of temperature becomes less. Other sources of error are imperfect stirring, which was guarded against by as vigorous a motion as possible, and the difficulty of estimating the temperature of the exposed thread of mercury, as this was not constant throughout. The last source of error is not so serious, as the total correction up to 40° is small, and a fairly large error in estimating the temperature of the bath is not important. The maximum error does not, we think, exceed 0·1° C.


Series I
Series II
Series I
Series II
T
log (t, - t)
t - (15 + 3T)
1.70
1.72
1.74
1.76
1.78
1.80
1.82
1.84
1.86
1.88
1.90
0
1
2
3
4
5
6
7
8
9
10
11
F.D. & S.O.R.

Two series of estimations were made: Series 1 with cream that had been kept in an ice-safe for eighteen hours, and Series 2 with cream that had been heated to 50° C. and cooled down to 15° as rapidly as possible; the cooling occupied about a quarter of an hour.

In Table 1 are given: *A*, the time of reading; *B*, the corrected temperatures; *C*, the differences between the temperature of the cream and that of the water (100·08° C.); *D*, the logarithms of the figures in column *C*; *E* the differentials of the figures in column *D*; and *F*, the differences between consecutive figures in column *B*, divided by the figures in column *C*.

We have plotted out on the plate* the figures in columns *B* and *D* against those in column *A*.

An inspection of the curves shows the following:

1. The curve of temperatures is continuous with the heated cream, but is discontinuous with the cooled cream; the point where discontinuity takes place is about 33° C.

2. The curve of the logarithms is nearly a straight line with the heated cream, and shows no well-marked break (if any at all); with cooled cream, on the other hand, the curve can only be expressed by two straight lines, with a well-marked break at about 34° C.

It is significant, though, considering the magnitude of the sources of error, not absolutely conclusive, that the rate of rise of temperature of cooled cream falls off about 33°-34°, as shown by the smaller figures; at these temperatures, in columns *E* and *F*, no falling off is noticed with heated cream.

We have also calculated the temperature (Table II.) at which the cream should be for each quarter-minute by a formula of the type log. $(t_1 - t) = K + cT$, where T = time, t_1 the temperature of the water, and t the temperature of the cream. We have had to use two formulæ in Series 1, (*a*) for the lower branch and (*b*) for the upper branch; the constants $c = 0{\cdot}01948$ and $0{\cdot}02172$ respectively. One formula suffices for Series 2, with a constant $c = 0{\cdot}02188$. The results for the first $2\frac{1}{2}$ minutes have been neglected in each case, as the introduction of the tube cooled the water somewhat, and the difference of temperature $t_1 - t$ was not steady till then.

It is seen in Series 1 that the point 34·49° lies equally well on both curves, and the values below all agree with the figures calculated by the lower formula within 0·10°; values above show a wider divergence. The values above agree equally well with the figures calculated by the upper formula, and values below show a very marked divergence from the figures calculated by this formula.

In Series 2 the agreement is almost as good throughout the curve, but it is to be remarked that the differences are all plus below 33, and all minus above; this, we think, clearly indicates a very slight break in the curve at this point, very much less than in Series 1, and not noticeable on plotting the curves, but still quite marked.

* As the scale of plotting necessary for reproduction would fail to show clearly the discontinuity of curvature in Series 1 if temperatures (t) and time (T) were plotted out against each other, the curves have been opened out by the substitution of the expression $t - (15 + 3T)$ for t. This does not change the character of the curves, but is equivalent to plotting them with obtuse-angled instead of rectangular co-ordinates.

TABLE II.

Series I.						Series II.		
Time.	Temp.	Temp. (Calc. *a*).	Diff.	Temp. (Calc. *b*).	Diff.	Temp.	Temp. (Calc.).	Diff.
2·5	24·25	24·17	−0·08			25·90	25·87	−0·03
2·75	25·10	25·03	−0·07			26·75	26·80	+0·05
3·0	25·92	25·85	−0·07			27·63	27·70	+0·07
3·25	26·70	26·69	−0·01			28·52	28·61	+0·09
3·5	27·48	27·51	+0·03			29·45	29·51	+0·06
3·75	28·22	28·31	+0·09			30·31	30·39	+0·08
4·0	29·02	29·11	+0·09			31·19	31·26	+0·07
4·25	29·90	29·90	—			32·11	32·13	+0·02
4·5	30·70	30·69	−0·01			32·93	32·95	+0·02
4·75	31·43	31·46	+0·03	31·08	−0·35	33·83	33·81	−0·02
5·0	32·21	32·25	+0·04	31·94	−0·27	34·69	34·65	−0·04
5·25	33·03	32·99	−0·04	32·78	−0·25	35·52	35·46	−0·06
5·5	33·76	33·73	−0·03	33·63	−0·13	36·32	36·27	−0·05
5·75	34·49*	34·47	−0·02	34·45	−0·04	37·18	37·07	−0·11
6·0	35·32	35·21	−0·11	35·26	−0·06	37·95	37·86	−0·09
6·25	36·14	35·92	−0·22	36·08	−0·06	38·69	38·63	−0·06
6·5	36·84 (?)	36·64	−0·20	36·86	+0·02	39·46	39·40	−0·06
6·75	37·68			37·65	−0·03	40·23	40·17	−0·06
7·0	38·49			38·42	−0·07	40·95	40·92	−0·03
7·25	39·26			39·20	−0·06			
7·5	39·95			39·96	+0·01			
7·75	40·65			40·68	+0·03			
8·0	41·43			41·44	+0·01			
8·25	42·10			42·16	+0·06			
8·5	42·84			42·88	+0·04			
8·75	43·56			43·60	+0·04			
9·0	44·29			44·30	+0·01			
9·25	45·03			44·99	−0·04			
9·5	45·69			45·66	−0·03			
9·75	46·35			46·35	—			
10·0	47·00			47·01	+0·01			
10·25	47·70			47·67	−0·03			
10·5	48·31			48·33	+0·02			
10·75	48·93			48·97	+0·04			
11·0	49·62			49·60	−0·02			
11·25	50·25			50·24	−0·01			
11·5	50·85			50·86	+0·01			

Considering the results, we conclude that:

1. With well-cooled cream a change in specific heat-capacity and a slight but distinct absorption of heat occurs at about 34°.

2. With heated cream rapidly (during $\frac{1}{4}$ hour) cooled a very slight change occurs at this point.

3. The only possible change which would produce these results is the melting of the fat.

4. As a final conclusion, the fat in well-cooled cream is solid; the fat in rapidly-cooled cream is still for the most part liquid or superfused, though there are distinct

* This point lies on both curves.

indications that a slight solidification has taken place in a quarter of an hour, and therefore the process of solidification is a slow one. The melting is practically instantaneous.

These conclusions are in complete accord with the density experiments previously referred to.

NOTES ON THE PROXIMATE ANALYSIS OF CLOVES.

By A. McGill, B.A., Inland Revenue, Canada.

(*Read at the Meeting, February* 5, 1901.)

Recorded analyses of genuine cloves (flower-buds of *Caryophyllustus aromaticus*) are not numerous. The following notes may therefore possess interest.

All the samples were procured direct from importers, and were ground by myself to a uniform degree of fineness. The classifications as Penang, Amboyna, and Zanzibar are based on the statements of the importers, but the grading in each class is based upon my own observation of the following physical characters: Colour, size, plumpness, retention of corolla, and freedom from stems. The best samples I have graded as first quality, the worse as second quality, and in a few cases, being unable with certainty to assign to either of these grades, I have given the number $1\frac{1}{2}$. This grading was made quite independently of the results of analysis, and it is interesting to observe how the physical characters of the whole clove give a suggestion as to its chemical character.

The most important constituent of cloves is the volatile or "essential" oil, and I have sought to modify the ordinary methods of working in such a way as to determine this component with the greatest degree of accuracy attainable by a practical, commercial process of assay.

The subjoined table gives percentage results obtained:

Penang Cloves.

No.	Moisture.	Total Volatile Matter.	Volatile Oil.	Total Extractive Matter.	Fixed Oil.	Quality.	Remarks.
1	5·0	21·2	16·2	28·2	12·0	1	
2	7·4	24·0	16·6	27·0	10·4	1	
3	5·8	20·7	14·9	24·4	9·5	2	Off colour, and resembled Zanzibar samples.
4	5·2	22·4	17·2	27·1	9·9	1	
5	6·9	21·7	14·8	26·5	11·7	1	
6	6·9	23·2	16·3	28·1	11·8	$1\frac{1}{2}$	A few stems.
7	7·1	24·3	17·2	28·2	11·0	1	
8	5·5	21·6	16·1	26·2	10·1	1	
Mean	6·2	22·4	16·2	27·0	10·8	—	Vol. oil : fixed oil :: 100 : 67.
				Amboyna Cloves.			
9	6·7	25·9	19·2	29·2	10·0	1	
10	5·5	23·5	18·0	26·7	8·7	1	
11	6·0	24·3	18·3	26·5	8·2	1	
Mean	6·1	24·6	18·5	27·5	9·0	—	Vol. oil : fixed oil :: 100 : 49.

ZANZIBAR CLOVES.

No.	Moisture.	Total Volatile Matter.	Volatile Oil.	Total Extractive Matter.	Fixed Oil.	Quality.	Remarks.
12	5·1	22·4	17·3	25·3	8·0	1	
13	6·0	24·3	18·3	28·1	9·8	1	
14	5·4	22·9	17·5	27·0	9·5	1	
15	5·7	18·4	12·7	21·3	8·6	2	Stems and shrunken buds.
16	6·3	22·9	16·6	26·3	9·7	1	
17	5·7	22·1	16·4	26·1	9·7	1	
18	6·5	18·6	12·1	22·3	10·2	2	Like No. 15.
19	6·5	21·0	14·5	25·2	10·7	2	,, ,,
20	6·2	23·6	17·4	27·8	10·4	1	
21	4·6	22·1	17·5	—	—	1	
22	4·1	21·4	17·3	—	—	1	
24	6·7	20·8	14·1	—	—	1½	Stems.
26	5·8	21·1	15·3	—	—	1½	,,
Mean	5·7	21·7	16·0	25·5	9·6	—	Vol. oil : fixed oil :: 100 : 59.
Mean, omitting 18	5·7	22·2	16·5	26·8	10·3	—	Vol. oil : fixed oil :: 100 : 62.

UNCLASSIFIED CLOVES.

23	7·5	17·4	9·9	—	—	2	West Coast cloves.
25	6·9	21·9	15·0	—	—	1	
27	4·4	16·7	12·3	—	—	2	
28	7·5	13·4	5·9	—	—	—	Clove stems.

As in all proximate work of this kind much depends upon details in the process employed, it is necessary to give the following particulars :

Recorded analyses of genuine cloves give water from 2·90 to 16·39 per cent. (König, " Zusammensetzung," etc., p. 744). It will be noted that I have not found so large a range as this, my extremes being 4·1 and 7·5 per cent.

On exposing samples of powdered cloves, *in vacuo*, over sulphuric acid, I found that loss of weight continued to occur for many days ; but that the rate decreased very rapidly after the first period of twenty-four hours, while the acid continued to grow deeper in colour till it became quite black from separated carbon. The subjoined table gives results obtained with six portions of 2 grammes of the same sample of cloves :

Hours in Desiccator.	Percentage Loss of Weight.							Remarks.
	a.	*b.*	*c.*	*d.*	*e.*	*f.*	Means.	
24	5·1	5·2	—	—	—	—	5·15	Acid scarcely discoloured.
48	5·4	5·7	5·5	4·6	5·1	4·8	5·15	,, distinctly brown.
72	5·8	6·1	5·8	5·1	5·2	5·2	5·55	,, more distinctly brown.
96	—	—	7·3	6·1	7·1	6·3	6·70	,, very brown.
120	7·9	8·2	—	—	—	—	8·05	,, very dark brown.
144	8·6	9·2	—	—	—	—	8·90	,, ,, ,,
	Desiccator 1.		Desiccator 2.					

The change in the rate of loss of weight, together with the fact that the volatile matter lost during the first twenty-four hours does not blacken the acid, leads me to conclude: (1) That water vapour only goes off during this period; (2) that loss of weight after the first twenty-four hours is essentially due to volatile oil. I found that at the end of sixteen days the total loss amounted to 11·45 per cent. The same sample of cloves lost 3·65 per cent. in twenty-four hours over sulphuric acid at ordinary pressure, and 4·72 per cent. in fifty-four hours, with only a slight discoloration of the acid. The advantage of drying *in vacuo* is chiefly the saving in time; but it is possible that the vapour tensions of water and essential oil of cloves are affected in such a way as to more sharply mark the point at which the oil comes off in notable quantity. In six samples treated in two desiccators of similar form, placed side by side, one being under atmospheric pressure, the other under 60 millimetres mercury, the following results were obtained for twenty-four hours:

	1.	2.	3.	4.	5.	6.
Reduced pressure ...	5·65	6·25	5·70	6·50	6·45	6·15
Ordinary pressure ...	4·65	5·15	4·65	4·85	4·95	5·20
Difference ...	1·00	1·10	1·05	1·65	1·50	0·95

Moisture, as given in the tabulated analyses, has been determined by exposure for twenty-four hours, over sulphuric acid under a reduced pressure of about 60 millimetres mercury.

Total volatile matter has been determined by exposure in a current of dry air at 98° C. for twenty-four hours. I find that a slight increase of volatile matter is obtained by previous treatment of the sample (in the capsule) with petroleum spirit. Two grammes of the sample are allowed to stand, at the ordinary temperature, after addition of 25 c.c. ether, until this ether is evaporated. It is then dried in the water-oven at 98° C. as described. Three samples gave results as below:

	1.	2.	3.
After ether treatment ...	20·72	21·52	9·47
Without ether	20·08	20·88	9·46
Difference	0·64	0·64	0·01

On repeating the treatment a further loss of weight occurred as follows: (1) 3·14, (2) 1·90 per cent. A third treatment yielded: (1) 0·46, (2) 0·30 per cent.; so that from 2 to 3 per cent. more volatile matter is obtained by a second treatment with ether. The results tabulated have been obtained by a single treatment as described.

The total extractive matter is obtained by Soxhlet extraction to constant weight. A check upon the volatile oil has been attempted by evaporating the solvent from this extractive, and drying, first at a low temperature and then at 100° C.; but it has been found impracticable to obtain constant weight, at either of these points, within 2 or 3 per cent. of error.

It is to be noted that, so far as the samples which would grade No. 1, on the

basis of their physical properties, are concerned, the maximum and minimum percentages of volatile oil are as follows :

	Max.	Min.	Mean.
Penang	17·2	14·8	16·2
Amboyna	19·2	18·0	18·5
Zanzibar	18·3	16·4	16·0
Mean, for a mixture of equal weights of the three kinds	18·2	16·4	16·9
Values found by C. Richardson	18·89	10·23	15·63

(Washington, Department of Agriculture, Bull. 13.)

The lowest value which I have found for any whole clove claiming to be genuine is 12·1 per cent. in No. 18. I am certain that neither this sample, nor Numbers 15, 19, 24, 23, or 27 would be considered other than low grade by dealers who are in the habit of handling cloves.

I am therefore of opinion that no sample of cloves claiming to be of good quality should yield less than 14 per cent. of volatile oil, when assayed by the method which I have described.

If total volatile matter is determined by treatment with petroleum spirit before drying at 100° C., this treatment being repeated, the minimum volatile oil found should be 16 per cent.

Discussion.

Mr. Chattaway said that the author's statement as to the percentage of oil in cloves was well borne out by work which he had himself done on this subject, though in a somewhat different way. On the Continent there were to be found plenty of synthetic volatile oils, the use of which for such purposes must certainly, he thought, be regarded as reprehensible, though he believed that some of them found their way into well-known preparations.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

A Rapid Method for the Detection of "Aniline Orange" in Milk. Hermann C. Lythgoe. (*Journ. Amer. Chem. Soc.*, xxii., 813.)—The test may conveniently be carried out on the portion of the milk which is to be tested for formic aldehyde. Fifteen c.c. of the milk are placed in a porcelain basin, an equal quantity of hydrochloric acid (specific gravity 1·20) is added, and the basin gently shaken. If the milk contains aniline orange the curd will be coloured pink, otherwise it will be white or yellowish. To test for formic aldehyde the same solution is boiled after the addition of a drop of a solution of ferric chloride, when a purple colour will appear if formaldehyde is present. Hydrochloric acid, to which ferric chloride

solution (5 c.c. of a 10 per cent. solution for 2 litres) has been added, may also be used for the two tests. The presence of both substances has no effect on either reaction.

Of the artificially-coloured samples of milk examined by the author during 1900, 48 per cent. contained aniline orange, and its use is on the increase. A. G. L.

The Determination of Lactose in Milk. A. Scheibe. (*Zeit. anal. Chem.*, 1901, xl., 1-14.)—After discussing the various methods of estimation, the author recommends the following processes :

Gravimetric Determination.—Twenty-five c.c. of the milk are diluted with 400 c.c. of water and treated with 10 c.c. of the copper sulphate portion of Fehling's solution (69·28 grammes per litre). After the further addition of 3·5 to 4 c.c. of normal sodium hydroxide solution and 20 c.c. of a cold saturated solution of sodium fluoride, the liquid is allowed to stand for thirty minutes, and then made up to 500 c.c. and filtered ; 100 c.c. of the filtrate are boiled for six minutes in a deep porcelain dish with 50 c.c. of Fehling's solution, the cuprous oxide reduced in hydrogen, and the corresponding lactose obtained from Soxhlet's table (ANALYST, xx., 228).

Polarimetric Determination.—To 75 c.c. of the milk are added 7·5 c.c. of 20 per cent. sulphuric acid and 7·5 c.c. of a solution of mercuric iodide, prepared by dissolving 40 grammes of potassium iodide in 200 c.c. of water, shaking the solution with 55 grammes of mercuric iodide, diluting to 500, and filtering the supernatant liquid.

The mixture is next diluted to 100 c.c., and filtered, and the filtrate polarized in a 4 d.c.m. tube at 17·5° C. With a Schmidt and Hänsch half-shadow apparatus provided with a double quartz compensation-wedge 1 degree corresponds to 0·16428 gramme of lactose in 100 c.c. When using a polarization apparatus with circular degrees and sodium light, the reading should be made at 20° C., and 0·4759 gramme of lactose per 10 c.c. calculated for each degree.

In correcting the error due to the volume of the precipitate the result may be multiplied by 0·94 in the case of whole milk (2·8 to 4·7 per cent. of fat), and by 0·97 in the case of skim milk. In making the correction for cream or colostrum it is essential to determine the volume of the precipitate in the following manner :

(*a*) Ten grammes of pure lactose are dissolved in 75 c.c. of water, and the solution mixed with 7·5 c.c. of 20 per cent. sulphuric acid and 7·5 of the mercuric iodide solution, diluted to 100 c.c., filtered and polarized. M_1 in the equation represents the amount of lactose in grammes thus found.

(*b*) Ten grammes of lactose are dissolved in 75 c.c. of milk with the aid of heat, the cold solution treated with 0·5 c.c. of concentrated ammonium hydroxide, and after ten minutes mixed with 7·5 c.c. of sulphuric acid (20 per cent.), and 7·5 of the mercuric iodide solution, diluted to 100 c.c., filtered and polarized. The difference between this reading and that obtained with 75 c.c. of the milk alone corresponds with the apparent amount of lactose added to the milk, or M_2 in the equation.

(*c*) The volume of the precipitate is calculated in the following manner : The

volume of the liquid + that of the precipitate (= NV) = 100 c.c. This volume corresponds to M_2; the volume of the liquid = 100 – NV, which corresponds to M_1, or

$$100 : M_2 = (100 - NV) : M_1$$
$$NV = \frac{100\ M_2 - 100\ M_1}{M_2}.$$

(*d*) The apparent amount of lactose in the milk multiplied by $\frac{100 - NV}{100}$ gives the actual amount. C. A. M.

The Detection of Cocoanut Oil in Butter. J. Wauters. (*Bull. de l'Ass. belg.*, 1901, xv., 25-28.)—In the determination of the Reichert-Meissl value a considerable proportion of insoluble fatty acids distil over with the volatile acids (*cf.* ANALYST, xxvi., 71).

The author has made general experiments in this direction, but has abandoned them in favour of the following method of distillation, in which the high temperature due to the concentration of the liquid being distilled is obviated.

Five grammes of the butter-fat are saponified, the soap dissolved in 150 c.c. of boiling water, 50 c.c. of 5 per cent. sulphuric acid introduced, and 100 c.c. of the liquid distilled in thirty to thirty-five minutes. The distillation is repeated after the addition of 100 c.c. of boiling water. The two distillates are filtered, and 50 c.c. of the filtrates titrated. The filters are washed with 50 c.c. of alcohol, and the washing mixed with the other 50 c.c. of the filtrates and again titrated.

In this way the following results, in c.c. of $\frac{N}{10}$ sodium hydroxide, were obtained :

	Soluble Volatile Acids.			Insoluble Volatile Acids.		
	1st Distillation.	2nd Distillation.	Total.	1st Distillation.	2nd Distillation.	Total.
Cocoanut oil	7·1	4·3	11·4	7·85	7·55	15·4
Butter, I.	22·4	5·4	27·8	0·6	0·3	0·9
,, II.	21·2	5·0	26·2	0·6	0·3	0·9
,, III.	23·8	5·2	29·0	0·4	0·4	0·8
Margarine	0·2	0·2	0·4	0·5	0·05	0·55
Mixture of 75 per cent. of butter (I.) and cocoanut oil, 25	18·4	5·8	24·2	2·8	2·2	5·0

The theoretical values for the mixture were: Soluble volatile acids, 23·7; and insoluble volatile acids, 4·55. C. A. M.

The Reichert-Meissl Value of Dutch Butter. L. T. Reicher. (*Zeit. angew. Chem.*, 1901, 125-129.)—The abnormal composition of Dutch butter in the autumn was attributed by van Rijn to the cows being left too long in the fields, and thus exposed to the influence of bad weather and changes of temperature, and he considered that abnormalities might be prevented by an earlier stalling.

This question has been further investigated in the State Laboratory at Amsterdam from 1894 to 1901. The butter was prepared each week from the mixed milk of eight cows during 1894-98, and of two herds of twenty and twenty-five respectively during 1898-1901.

During the autumn months Reichert-Meissl values lower than at other times of the year were obtained, whilst the rise observed by van Rijn after stalling also occurred in the majority of cases. C. A. M.

The Detection of Archil in Wine. R. Truchon. (*Ann. de Chim. Anal.*, 1900, v., 444, 445.)—Fifty c.c. of the wine are acidified with 1 c.c. of 10 per cent. sulphuric acid and boiled for five minutes with a little wool, which is then washed and immersed in ammoniacal water. In the case of natural wines the wool assumes a green tint, whilst if the wine contained archil it becomes violet, the intensity of the shade depending on the quantity of colouring matter. C. A. M.

Detection of Foreign Colouring Matter in Spirits. Second Method. C. A. Crampton and F. D. Simons. (*Journ. Amer. Chem. Soc.*, xxii., 810.)—The authors prefer the following method to their first one (*Journ. Amer. Chem. Soc.*, xxi., 355),* which depends on the absorption of caramel by Fuller's earth. The present method is based on the insolubility in ether of the foreign colouring matter of caramel and prune-juice, the natural colouring matter of oak-wood being readily soluble in ether. Fifty c.c. of the sample are evaporated on the water-bath nearly to dryness; the residue is washed into a 50 c.c. graduated flask, and 25 c.c. of absolute alcohol are added; the solution is then made up to the mark with water. Twenty-five c.c. of this solution are then transferred to a separating funnel, and shaken up with 50 c.c. ether at intervals for half an hour. A special separating apparatus is used, having two bulbs connected by a long stem, on which is the graduating mark of the lower bulb, which holds exactly 25 c.c.; the upper bulb has a capacity of about 100 c.c. When the extraction is finished, the lower layer is again made up to 25 c.c. with water. The two layers are again mixed; the lower one is drawn off, and its colour compared in a tintometer with that of the other 25 c.c. of the original solution. The amount of colour extracted by the ether is then calculated in percentages. To obtain accurate results, the conditions given should be carefully adhered to.

In a series of thirty-four naturally-coloured spirits subjected to the above treatment, on an average 41·7 per cent. of the colour was removed by the ether (max. 51·1, min. 36·4 per cent.). In a series of seventeen artificially-coloured spirits, on an average 14·8 per cent. was removed (max. 23·2, min. 0·0 per cent.). A. G. L.

The Assay of Coca. W. R. Lamar. (*Amer. Journ. Pharm.*, 1901, lxxiii., 125-131.)—In the author's opinion, the main cause of the many discordant results obtained in the analyses of this drug is the want of appreciation of the instability of the various alkaloids.

* Analyst, xxiv., 207.

Cocaine, cinnamyl-cocaine and isatropyl-cocaine are all methyl esters of ecgonine, and the methyl group attached to the carboxyl is readily split off, forming, in the case of cocaine, benzoyl-ecgonine, which still possesses alkaloidal properties, but is practically insoluble in the ordinary solvents used to extract the alkaloids from their alkaline solution.

To obviate this, it is essential to avoid a large excess of alkali, and to have this of the lowest possible strength capable of completely liberating the bases.

The author has found petroleum a suitable solvent for extracting the alkaloids, since it removes the smallest possible amount of other matters. The following modification of E. Squibb's process is recommended :

Twenty-five grammes of the powdered leaf are well mixed with 25 c.c. of a 2 per cent. solution of ammonia, and left in a covered vessel for thirty minutes with an occasional stir. Then, if the odour of ammonia is still perceptible, 75 c.c. of petroleum are introduced little by little, with continual stirring, and the whole macerated for an hour or more, being stirred every ten to fifteen minutes.

The contents of the jar are next transferred to a percolator, the last portions of leaves being washed out with petroleum, fresh supplies of which are added when necessary, and about 450 c.c. of percolate collected. The percolate is shaken in a separating funnel with 25 c.c. of $\frac{N}{10}$ hydrochloric acid for ten minutes, the acid liquid withdrawn, and the shaking repeated twice more with the same quantities of acid. The united acid extracts are shaken with 20 c.c. of ether, and subsequently with a fresh portion of 15 c.c. of ether, so as to eliminate the last traces of petroleum and colouring matter.

The acid solution is then transferred to a third separating funnel. The ether in the first funnel is shaken twice with 5 c.c. of water, and the aqueous layers added to the ether in the second funnel, whence, after shaking and separating, they are drawn off into the third funnel, containing the main solution.

Sufficient ammonia solution (10 per cent., diluted with four times its volume of water) to render the liquid alkaline is now introduced, about 8 or 9 c.c. being required. The alkaloids are then extracted with successive portions of 40, 30 and 30 c.c. of ether, the united extracts evaporated in a weighed beaker at 30° to 35° C., and the residue dried at 60° C. until constant in weight. The alkaloids thus obtained are crystalline and nearly colourless. As a check upon the weight, they may be titrated by using an excess of $\frac{N}{20}$ sulphuric acid, and titrating the excess of acid with $\frac{N}{20}$ potassium hydroxide solution using cochineal tincture as indicator. The mean factor for the alkaloids, as found in numerous experiments, was 0·01514 gramme for each c.c. of $\frac{N}{20}$ sulphuric acid.

A. Dohme (*Amer. Pharm. Assoc.*, 1895, 268) claimed that the Keller method was the best method of assaying coca. The author, however, finds that although the latter method gives higher gravimetric results, it gives much lower ones by titration, and the alkaloids are dark brown in colour and crystallize with difficulty. This is attributed to the mixture of chloroform and ether extracting substances which the petroleum does not. From numerous assays the author concludes that coca-leaves of good quality should yield, by the process described above, about 0·7 per cent. of total alkaloids.

C. A. M.

Commercial Assafœtida. M. I. Wilbert. (*Amer. Jour. Pharm.*, 1901, lxxiii., 131-135.)—The author has obtained the subjoined results in the examination of different samples of the drug as sold in the American market:

Description.	Soluble in Alcohol per cent.	Insoluble in Alcohol per cent.	Ash per cent.
1. Loose tears	70·1	29·9	7·2
2. Lump	44·3	55·7	34·2
3. Choice gum	41·4	58·6	35·8
4. Mass tears	36·4	63·6	45·1
5. Lump	31·2	68·8	51·9
6. ,, ...	30·2	69·8	50·6
7. Powdered	28·5	71·5	46·6
8. ,, ...	19·8	80·2	60·6
9. Soft mass	18·3	81·7	62·1
10. Old gum	40·5	59·5	45·9

The author considers that the American drug is grossly adulterated, and seldom complies with the Pharmacopœial requirements. C. A. M.

ORGANIC ANALYSIS.

A Generally Applicable Volumetric Method for the Determination of Aldehydes. Maximilian Ripper. (*Monatshefte f. Chem.*, xxi., 1079.)—The method is based on the combination of alkaline bisulphites with aldehydes. Twenty-five c.c. of the solution to be examined, which should not contain more than $\frac{1}{2}$ per cent. of the aldehyde, are run into 50 c.c. of a solution of potassium bisulphite containing 12 grammes $KHSO_3$ per litre, placed in a 150 c.c. flask, which is then securely corked, and allowed to stand for a quarter of an hour. During this time another 50 c.c. of the potassium bisulphite solution are titrated with decinormal iodine solution. The excess of bisulphite added to the aldehyde solution is then determined with the same iodine solution, and from the difference the amount of aldehyde present is calculated.

Solutions of potassium bisulphite stronger than the above should not be employed, as the larger quantities of hydriodic acid formed would exert a reducing action on the sulphuric acid formed. The use of alcohol to dissolve the aldehyde should also be avoided as far as possible, as even relatively small quantities of alcohol (upwards of 5 per cent.) prevent the iodide of starch reaction. With the very dilute solutions of aldehyde used, however, a very small addition of alcohol will be sufficient in most cases.

The method was tried with formaldehyde, acetaldehyde, benzaldehyde, and vanillin. For the last three, the author prepared the pure aldehydes from commercial specimens, and then made up solutions of known strength. In the case of formaldehyde, he used the hexa-methylene-tetramine method to check his results. In all cases satisfactory results were obtained. A. G. L.

The Valuation of Commercial Solutions of Lactic Acid. F. Jean. (*Ann. de Chim. Anal.*, 1900, v., 285, 286.)—From 5 to 10 c.c. of the solution are used for the determination of the total acidity in terms of sulphuric acid.

A similar quantity of the sample is evaporated on the water-bath, the residue mixed with 10 c.c. of water, and again evaporated, this process being once more repeated, so as to expel all volatile acid. The fixed acidity is then determined in the residue.

From 5 to 10 c.c. of the original solution are evaporated to dryness, the residue taken up with water, and the liquid brought to boiling-point, and neutralized with precipitated barium carbonate added little by little. The filtrate is evaporated in a platinum basin, and the residue ignited at a moderate temperature, so as to convert the barium lactate into carbonate. It is then treated with boiling water, and the insoluble portion collected on a filter, and washed with boiling water until the washings cease to be alkaline. A definite quantity of standard hydrochloric acid is then run on to the filter, so as to dissolve the barium carbonate, and the filtrate, after being boiled, titrated with standard alkali, the result giving the amount of hydrochloric acid neutralized by the barium carbonate derived from the barium lactate.

Ten c.c. of $\frac{N}{10}$ hydrochloric acid correspond to 0·09 gramme of lactic acid.

C. A. M.

Separation of Oxalic Acid from Tartaric Acid. M. Palladini. (*Gazz. Chim. Ital.*, 1900, xxxii., [2], 446; through *Chem. Zeit. Rep.*, 1901, 33.)—When attempts are made to separate these acids by precipitating with calcium chloride in presence of acetic acid, the calcium oxalate carries some tartrate down with it; and the latter cannot be entirely extracted, even by boiling with a large excess of acetic acid. The process is therefore not adapted for quantitative purposes. F. H. L.

Examination of Wax. (1) J. Werder. (*Chem. Zeit.*, 1900, xxiv., 967.) **(2) K. Dieterich.** (Analyst, 1897, xxii., 242.)—Werder finds that the Hübl prescription —*i.e.*, heating 5 grammes of wax for forty-five minutes on the water-bath with alcoholic alkali—is not sufficient to insure thorough attack of the beeswax; and by operating in this manner, he shows that the saponification value, the ester number, and the "ratio" are not given correctly. He recommends boiling the mixture for one hour in a flask with inverted condenser over a naked flame and wire-gauze. By taking 5 grammes of wax, 25 c.c. of seminormal potash, and 20 c.c. of 95 per cent. alcohol, the process can be combined with Weinwurm's qualitative test for paraffin and ceresin (Analyst, 1897, xxii., 242), for the reaction appears with less than 5 per cent. of either adulterant when the alcoholic liquid is diluted with hot water, and there is no necessity to remove the spirit and add glycerin as proposed by Weinwurm.

By weighing the amount of matter soluble in ether after saponification of bleached or unbleached wax, the proportion of paraffin or ceresin may be determined, for after examining some twenty samples of genuine wax, the author finds that between 48·55 and 53·01 per cent. of unsaponified matter always remains. Two grammes of the

sample are boiled as above with 5 c.c. of normal potash and 15 c.c. of alcohol, the solution is concentrated in a basin to about 15 c.c., the residue mixed with sand, dried, and extracted for three hours with pure dry ether, drying the fat for one hour at 100° C. Occasionally the wax may contain so little unsaponifiable matter that an addition of 5 per cent. of ceresin or paraffin might not be shown by this quantitative process; but its presence would be indicated by the qualitative test.

Dieterich agrees that the Hübl directions are unsatisfactory. In the interest of rapidity, he prefers to use only 3 grammes of wax, and to boil for half an hour. Both authors regret that some standard methods of analysing wax have not been decided upon, regarding uniformity as important. F. H. L.

Notes on the Estimation of Pentosans. G. Kröber. (*J. Landwirthsch.*, 1901, xlviii., 357; through *Chem. Zeit. Rep.*, 1901, 40.)—The author has submitted the hydrochloric acid and phloroglucinol method of estimating pentosans to a further examination. He finds that the presence of di-resorcinol in the phloroglucinol is absolutely without influence on the weight of phloroglucide obtained. The latter should be dried for four hours; and as it is very hygroscopic, it must be weighed in a closed tube. Repeated or slow desiccation does not alter its weight, provided moisture be excluded. Exposed to the air, the phloroglucide gains in weight, and retains that gain even when dried once more. This, however, is due to the fact that it oxidizes somewhat during the second drying, and therefore it must certainly oxidize a little during the first desiccation. The solubility of the phloroglucide in 550 c.c. of liquid (400 c.c. of dilute hydrochloric acid and 150 c.c. of water) is 5·1 to 5·2 milligrammes. Ninety-six parts of furfural give 184·9 parts of phloroglucide; and this is practically the theoretical yield, the molecular weight of the substance being 186 ($C_{11}H_6O_3$). Only the one condensation product is formed between phloroglucinol and furfural. The original paper includes tables for converting the yield of phloroglucide into furfural, arabinose, or xylose, with the corresponding quantities of pentosans, etc. F. H. L.

Volumetric Estimation of Tannin. L. Specht and F. Lorenz. (*Chem. Zeit.*, 1901, xxv., 5.)—This article describes certain modifications and further investigations into the method already recorded (Analyst, 1900, xxv., 163). To simplify the process, and to eliminate the disturbing influence of the oxygen dissolved in the water, the operation is conducted as follows: 0·45 gramme of tannin, 0·54 gramme of tartar emetic, and 0·90 gramme of safranine, are precipitated in 1,500 c.c. of water; and then 35 c.c. of sodium bisulphite and 33 c.c. of sodium bicarbonate, each in 10 per cent. solutions, are added. The titration, etc., remains as before prescribed.

Thus carried out, the method generally gives high results which vary in inaccuracy according to mass conditions. The present paper contains a mathematical investigation of the sources of error, and formulæ for their separate elimination. Briefly, the combined errors may be removed by the use of the annexed table:

True Tannin, per Cent.	Tannin by Analysis, per Cent.	Correction per 0·5 per Cent.
100	100·0000	
		0·37823
95	96·2177	
		0·39294
90	92·2883	
		0·40682
85	88·2201	
		0·42016
80	84·0185	
		0·43240
75	79·6945	
		0·44395
70	75·2550	
		0·45510
65	70·7040	
		0·46590
60	66·0450	

The table is employed thus: With a tannin of known purity (100 per cent.), titration shows that the "lake" contains (say) 0·68712 gramme of safranine. The same weight of tannin to be examined gives a lake containing (say) 0·54803 gramme of dye; whence its percentage purity is (0·68712 : 0·54803 : : 100 :) 79·757. Applying the correction in the table, this becomes

$$75+\frac{79{\cdot}757\times 79{\cdot}6945}{0{\cdot}4324}\times 0{\cdot}5=75{\cdot}072 \text{ per cent.}$$

The titration requires some experience to carry out successfully, for at first the operator is apt to use too much hydrosulphite. The liquid needs stirring as thoroughly as possible without causing the formation of bubbles. With low-grade specimens it is advisable to increase the weight taken until the amount of true tannin present roughly corresponds to that in the standard sample. The method has only been studied from the dyer's and printer's point of view, and on such materials only as are commonly employed by them. F. H. L.

The Detection of Antithermic Substances in Urine. A. Petermann. (*Ann. de Chim. Anal.*, 1901, vi., 4-6.)

Salicylic Acid given in the Form of Sodium Salicylate, or Salol.—These are taken as typical of the compounds of salicylic acid which are decomposed in the animal organism with the liberation of salicylic acid. The urine should be rendered slightly acid, but too much acid interferes with the ferric chloride test, and may produce by itself a reddish-orange colour. One drop of a 10 per cent. solution of ferric chloride is added to 25 c.c. of the urine.

Antipyrine.—When the urine, tested as described above, gives, instead of a violet coloration, a blood-red colour, which disappears on the addition of an excess of acid or alkali, the presence of antipyrine is probable. It is confirmed by extracting the urine with chloroform or benzene.

Colouring Matters of the Urine.—Not infrequently urine gives a coloration with ferric chloride which might be confused with the reactions for salicylic acid and antipyrine. It differs from these, however, in not being destroyed by hydrochloric acid, and in eventually yielding under the above conditions a precipitate of the same colour. C. A. M.

Quantitative Reactions distinguishing between Petroleum and Brown Coal-Tar Pitch, and the Pitchy Residue from the Distillation of Fats. D. Holde. (*Berichte*, 1900, xxxiii., 3171-3175.)—Although the hard pitchy residues left on distilling fats contain only a trifling proportion of free fatty acids and esters, it is possible to concentrate these by extracting the substance with a mixture of alcohol and ether, and then to obtain solutions giving considerable higher acid and ester values than the corresponding extracts of petroleum and brown coal-tar pitches.

About 20 grammes of the pitch are dissolved, as far as possible, in 80 c.c. of ether eventually by boiling under a reflux condenser. The bulk of the neutral black constituents are precipitated by the addition of absolute or 96 per cent. alcohol, the liquid filtered after some time, and the filter washed with a mixture of alcohol and ether.

The filtrate is evaporated, and the residue dried and weighed. It is then re-dissolved in ether containing a little alcohol, and the acid value determined by titration with $\frac{N}{10}$ alkali.

The ester value is determined by evaporating the solution and boiling the residue with 25 c.c. of $\frac{N}{10}$ alcoholic alkali and 25 c.c. of benzene, and titrating the excess of alkali with hydrochloric acid. A 2 per cent. alcoholic solution of alkali blue 6*b* is used as indicator, and the end-point found by shaking the liquid in a flask, and noting the colour of the liquid running down the sides.

As a further test the pitch is distilled either alone or with superheated steam, in which process the fatty acids are concentrated in the first fraction (one-fourth) of the distillate, which consequently gives a higher acid value than that of the corresponding fraction from petroleum or tar-pitch.

The following results were thus obtained:

Dry Distillation. Acid Values.

	Fraction I. About one-fourth.	Fraction II. About one-half.	Fraction III. About one-fourth.
Hard wool-fat pitch ...	5·2	1·1	0·08
Mixture of hard fat pitches	5·3	0·95	0·6
Hard petroleum pitch ...	0·4	0·4	0·3
Brown coal-tar pitch ...	0·1	0·2	0·4
Brown coal-tar pitch II. ...	0·2	0·6	0·6

Distillation with Superheated Steam. Acid Values.

	Fraction I.	Fraction II.	Fraction III.
Mixture of hard fat pitches	14·6	13·7	13·4
Soft wool-fat pitch ...	34·8	37·8	7·0

The author remarks that all the fat-pitches examined by him contained traces of copper derived from the copper distillation vessels, whilst the petroleum pitches (which are distilled in iron vessels) were all free from copper. C. A. M.

INORGANIC ANALYSIS.

The Separation of Cerium Earths in Monazite Sand. R. J. Meyer and E. Marckwald. (*Berichte*, 1900, xxxiii., 3003-3013.)—From the results of their experiments with different methods the authors recommend the following process as the most suitable. The original material used by them was purchased as "cerium oxalicum oxydul pur." containing about 25 per cent. of water.

Conversion of the Oxalates into Soluble Nitrates.—When the oxalates are ignited in air, a mixture of oxides is obtained, the solubility of which depends upon the proportion of cerium, and which can only be dissolved with great difficulty when certain other substances are present. This can be obviated in the following way: On boiling the mixed oxalates with potassium hydroxide solution in the presence of hydrogen peroxide, the oxalic acid is completely eliminated, and a yellow crystalline precipitate is obtained, consisting of a mixture of ceric hydroxide with higher oxides ($?CeO_3$). This is drawn off by suction, washed, dried at 120° C., and dissolved in concentrated nitric acid, yielding a dark-red solution. The drying at 120° C. must be continued for some time in order to destroy the cerium peroxides, since these would subsequently act like hydrogen peroxide and reduce the ceric solution.

If it is not desired to obtain a solution containing the cerium in the tetravalent condition, but to oxidize it subsequently as in the method of Witt and Theel, the oxalic acid is best removed by boiling the mixed oxalates with concentrated nitric acid. For this purpose the oxalates are gradually introduced into twice their weight of nitric acid (specific gravity 1·4), which is boiled, with the addition of a few drops of nitric acid from time to time, until the evolution of gas has ceased. Intermediate products consisting of compounds of oxalates and nitrates are first formed, and if the boiling has not been continued long enough, separate out on cooling.

To the brown solution of nitrates thus obtained ammonium nitrate is added in the proportion of 80 grammes to 100 grammes of the original mixture, and on evaporating the liquid to a third of its volume, the double nitrates crystallize out. They are much less hygroscopic and less soluble than the simple nitrates. The crystals are dissolved in water, and the solution used for the separation of ceria.

Separation and Purification of Ceria.—In the authors' opinion the method of O. N. Witt and W. Theel (*Berichte*, xxxiii., 1315) is likely to completely supersede the older methods. They have not succeeded, however, in completely freeing the precipitate (which contains the entire cerium in the form of basic sulphate) from other earths by washing. The washed precipitate, which consists of basic ceric sulphate and calcium sulphate, with traces of didymium and lanthanum salts, is dried at 120° C., powdered and dissolved in ten times its weight of hot concentrated nitric acid (1·4), which has previously been freed from nitrous oxides by boiling. Ammonium nitrate dissolved in a little water is added to the dark-red solution in the proportion of about one and a half times the quantity of the dissolved precipitate, and the double nitrate $[(NH_4)_2Ce(NO_3)_6]$ soon crystallizes out, a further portion being obtained on evaporating the mother-liquid. The double nitrate is purified by recrystallizing once

or twice from concentrated nitric acid (1:4), drained by suction on a platinum cone, and dried over sulphuric acid and potassium hydroxide.

Separation of the Yttrium Earths.—As monazite sand only contains small quantities of these, it is sufficient to effect the separation by the addition of finely pulverized potassium sulphate to the *boiling* solution (Muthmann and Rölig, *Berichte*, xxxi., 1722). The filtrate from the cerium precipitation is heated to boiling, and a strong current of steam introduced, whilst the potassium sulphate is introduced little by little, until a spectroscopic test of the solution shows that didymium has practically disappeared. About 125 grammes of potassium sulphate are required for 400 grammes of the original crude oxalate. The clear supernatant liquid is decanted whilst hot, and the precipitate washed several times with a cold aqueous solution of potassium sulphate, dried, and weighed.

Conversion of the Double Sulphates of Didymium and Lanthanum into Nitrates.—The method which the authors have found to be the most simple is to boil the sulphates for a short time with five times their weight of concentrated nitric acid. The entire mass is rapidly poured into boiling water (1500 c.c. to 100 grammes of sulphates), and the clear solution thus obtained treated with ammonium oxalate (75 grammes to 100 grammes of sulphates), and then neutralized with concentrated ammonium hydroxide. The precipitated oxalates are withdrawn by suction, introduced into one and a half times their quantity of concentrated nitric acid, and converted into nitrates, as described above. The acid solution of nitrates is evaporated in the water-bath until nitric acid ceases to be evolved. The residual syrup is dissolved in hot water and diluted to a litre.

Separation of Didymium and Lanthanum.—In the authors' opinion the method of Muthmann and Rölig (*loc. cit.*) is the most simple and exact for this purpose. It consists in fractionally precipitating the boiling, nearly neutral, solution of didymium and lanthanum with magnesia, in which process the didymium earths, being the less basic, are precipitated first. This precipitation should be twice repeated.

The sample of crude oxalate thus analysed by the authors had the following composition: Water, 25·0; cerium oxalate (anhydrous), 32·5; didymium oxalate (anhydrous), 21·5; lanthanum oxalate (anhydrous), 14·0; and yttrium earths and loss, 7·0 per cent. C. A. M.

Irregular Distribution of Sulphur in Pig Iron. Randolph Bolling. (*Journ. Amer. Chem. Soc.*, xxii., 798.)—To study the irregular distribution of sulphur in pig-iron, a rod 12 × 14 inches, and weighing about 10 pounds, was cast (vertically) in sand. Eight holes were drilled at intervals of $1\frac{5}{8}$ inches, starting from the bottom, and sulphur determined by the cadmium chloride method. The results expressed in percentages were: 0·023, 0·03, 0·032, 0·036, 0·036, 0·036, 0·036, 0·036, showing a difference of 0·013 per cent. between the upper and lower surface. To obtain a true sample, it would consequently be necessary to drill a hole right through the rod, and mix the drillings well. In another case, drillings from the top surface showed 0·075 per cent. sulphur, whilst drillings from a hole through the sample gave 0·045 per cent. A. G. L.

A Method for the Rapid Determination of Carbon in Steel. Robert Job and Charles T. Davies. (*Journ. Amer. Chem. Soc.*, xxii., 791.)—The authors have simplified G. W. Sargent's method (ANALYST, xxv., 302). The combustions are carried out in a porcelain tube 20 inches long, which is heated by three burners having spreaders on their tops, and contains a roll, 4 inches long, of oxidized copper gauze, kept in position by placing pieces of clay-pipe stems between it and the end of the tube. The products of combustion pass first through a U-tube, one limb of which is filled with anhydrous cupric sulphate, the second limb containing anhydrous cuprous chloride. This tube may be regenerated by heating whilst applying a gentle suction. The gases then pass through a bubble-tube containing 5 to 10 c.c. of a solution of silver sulphate in sulphuric acid (specific gravity 1·40), which is refilled if any precipitate forms; next through a calcium chloride tube, and then into the weighed potash bulbs. To prevent the boats from cracking the tube, a cylinder of platinum foil is placed in the tube.

Oxygen free from hydrocarbons is readily obtainable, and need only be passed through potash bulbs to purify it. Should it be necessary, however, to pre-heat it, this may be done in a copper tube placed in the same furnace above the porcelain tube. During the first part of this combustion oxygen is passed at the rate of four bubbles per second for seven minutes, and then air at the rate of six or seven bubbles per second for twelve and a half minutes. Three weighed bulbs are used for a set of determinations. The bulbs are allowed to stand for forty minutes in the balance-case before weighing. A. G. L.

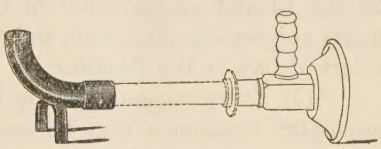
Kilgore's Modification of the Volumetric Method of estimating Phosphoric Acid in Fertilizers. C. B. Williams. (*Journ. Amer. Chem. Soc.*, xxiii., 8.)—By this method the author was able to deal with thirty samples daily with great facility. For totals, 2 grammes of the fertilizer are boiled down with 30 c.c. concentrated nitric acid and 10 c.c. hydrochloric acid in a 200 c.c. flask to a concentration of 8 to 10 c.c., unless the sample contains much iron and alumina, in which case it is first boiled for half an hour with 30 c.c. hydrochloric acid, 30 c.c. nitric acid are then added, and the boiling continued until the excess of hydrochloric acid is removed. After cooling, the solution is made up to the mark and filtered, or allowed to clear by standing. Twenty c.c. are then measured into a 500 c.c. Erlenmeyer flask, and 10 to 12 grammes ammonium nitrate and 50 c.c. water added; the excess of acid is neutralized with ammonia, and, when cold, 30 c.c. of clear molybdic solution are added, and the flask is placed in a shaking machine, maintained at forty-five to fifty-five revolutions per minute, for thirty minutes. The solution is then filtered through a perforated porcelain disc covered with asbestos, and placed in a carbon filter, and flask and precipitate thoroughly washed. The outside of the filter is then washed free from acid, the filter inverted over the flask in which the precipitation was effected, and the disc and asbestos are then pushed into the flask by means of a copper-wire rigidly connected to the disc, and reaching through the stem of the funnel. The contents of the flask are then titrated, using solutions of potassium hydroxide and nitric acid, 1 c.c. of which corresponds to 0·5 milligramme of phosphoric acid.

For insolubles, 40 c.c. of solution are taken; the process is carried out as above, except that little or no water is added before precipitation.

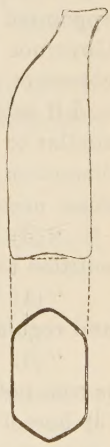
A large number of determinations were made, in which the above method was compared with the official gravimetric method. In all instances the results were extremely satisfactory. A. G. L.

APPARATUS.

A Burner for Use in Confined Situations. W. Burstyn. (*Oesterr. Chem. Zeit.*, 1900, iii., 518.)—As shown by the cut, this device consists of a brass "bend," with socket attached, which can be slipped over an ordinary Bunsen when laid on its side. With its aid vessels can be heated that are more conveniently placed close to the bench, while it also permits the flames of several burners to be brought quite close together. F. H. L.



A New Shape for Reagent Bottles. B. Setlik and J. Fric. (*Chem. Zeit.*, 1900, xxiv., 1138.)—The construction of these bottles is shown in elevation and cross-section by the annexed illustration. It is easier to pour from them when they are quite full; to obtain single drops of liquid from them; to empty them to the last drop; and to charge burettes and similar narrow vessels from them, than with the ordinary cylindrical bottles having concentric necks. F. H. L.



BUREAU OF MINES AMENDMENT ACT OF BRITISH COLUMBIA.

This Act, which forms a new and important departure in legislation, is given *in extenso*. So far as British Columbia is concerned, analytical chemists are placed on a par with the members of the legal and medical professions, insomuch that no analyst henceforth will be allowed to practise in that colony unless he has satisfied the examiners appointed under the Act as to his skill and competence. The principle involved is one that might be adopted in other countries with advantage.

CHAPTER XI.

AN ACT TO AMEND THE "BUREAU OF MINES ACT."

27th February, 1899.

Her Majesty, by and with the advice and consent of the Legislative Assembly of the Province of British Columbia, enacts as follows:

1. This Act may be cited as the "Bureau of Mines Act Amendment Act, 1899."

2. Section 12 of Chapter 36 of the Revised Statutes, 1897, is hereby repealed, and the following substituted therefor:

"12. (1) The Minister shall, twice or oftener in each year, institute an examination for efficiency in the practice of assaying and other kindred subjects as may be deemed advisable; the examination shall be conducted by examiners to be appointed by the Minister; each candidate shall pay, before the examination, such fee as may be determined by the Lieutenant-Governor in Council, who shall grant a certificate of efficiency to each successful candidate at such examination, on the recommendation of the duly appointed examiners, and the payment of a further fee to be determined by the Lieutenant-Governor in Council, such certificate, and the certificate issued under sub-section (2) hereof, to be taken as *primâ facie* evidence of efficiency in any Court of Law in the Province.

"(2) Every person applying for a certificate of efficiency, on satisfying the duly appointed examiners that he has passed a course of practical analytical or assay work in any School of Mines or College in Canada, Great Britain, or Ireland, shall be entitled to receive a certificate of efficiency on the recommendation of the duly appointed examiners, and on payment of a fee to be determined by the Lieutenant-Governor in Council; but it shall rest with the examiners to decide whether such course or examination is equivalent to the examination prescribed by the examiners, and if such examination or course is not, in the opinion of the examiners, sufficiently similar to the examination required by the examiners, the examiners may, in their discretion, require such candidate to pass such further examination as they may deem necessary.

"(3) The examiners appointed by the Lieutenant-Governor in Council shall be entitled to receive a certificate of efficiency.

"(4) The Lieutenant-Governor in Council may from time to time prescribe rules and regulations for the carrying out of such examinations.

"(5) After the expiration of two years from the first day of March, A.D. 1899, no person not holding a certificate of efficiency as prescribed in sub-sections (1), (2), and (3) hereof shall, by public advertisement or otherwise, solicit employment as an assayer, or to perform assays, nor shall any such person ask or receive payment for performing any assay, nor shall any such person give a written statement of the result of any assay performed by him: Provided that nothing in this sub-section shall apply to persons who already hold a certificate of efficiency under the examination prescribed by section 12 of the 'Bureau of Mines Act.'

"(6) Any persons violating the provisions of this section shall be liable to a fine of not less than twenty-five dollars and not exceeding one hundred dollars for each offence."

APPOINTMENT.

Mr. J. CUTHBERT WELCH, of Trail, has been appointed one of the three examiners under the Bureau of Mines Amendment Act of British Columbia of 1899.